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(71) Applicant
Bowthorpe-Hellermann Limited

(Incorporated in the United Kingdom)

Gatwick Road, Crawley, Sussex, United Kingdom

(72) Inventor
Edward Cole

(74) Agent and/or Address for Service
Urquhart-Dykes & Lord
Alexandra House, Alexandra Rd, Swansea,
West Glamorgan, SA1 5ED, United Kingdom

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(54) Flame retardant polymer compositions

(57) The composition comprises a blend of polyethylene and an ethylene-vinyl acetate copolymer having a hydrated mineral flame retardant dispersed therein, the composition further containing an oligomeric polyester resin dispersant. The hydrated mineral flame retardant is typically aluminium hydroxide, optionally together with magnesium hydroxide.

Artefacts made from the composition are useful for protecting electrical and fibre optical cables where stringent flame resistance properties are required.

Flame Retardant Polymer Compositions

The present invention is concerned with flame retardant polymer compositions and, in particular polymer compositions containing mineral flame retardants.

The use of halogenated organic additives to impart flame retardancy to polymer compositions is well established. Formulations containing such additives suffer from the drawback that they generate corrosive gases and high levels of smoke during pyrolysis. As a result, mineral fillers such as hydroxides of aluminium and magnesium are increasingly being used as flame retardants and smoke suppressants. These mineral fillers are, however, comparatively inefficient as flame retardants, and for this reason loadings in excess of 35% by weight are usually required to give useful flammability.

With such highly filled formulations, mechanical properties such as the elongation at break, flexibility and impact strength are detrimentally affected. This deleterious influence is, in part, generally attributed to uneven dispersion of the additive and a poor particle-polymer interfacial linkage. Surface-treated mineral flame retardants and processing aids (e.g. stearic acid and low molecular weight polyalkene lubricants) have given moderate improvement in some properties. In curable formulations, such additives may play a role in the cross-linking reaction.

We have now found that by using certain polymeric dispersants, a cross-linked formulation may be effectively flame retarded with very high loadings (for example 60% by weight) of inorganic flame retardants without serious loss of tensile elongation properties. Surprisingly, such formulations also retain much of their flexibility and softness.

According to the present invention there is provided a curable, flame retardant polymer composition which comprises a blend of polyethylene and an ethylene-vinyl acetate copolymer having a hydrated mineral flame retardant dispersed therein, the composition further containing an oligomeric polyester resin dispersant. The oligomeric polyester dispersant is typically a material commercially available from I.C.I. Speciality Chemicals under the trade name FYPERMER FP1. The amount of the polyester is typically 1-10% by weight (based on the total filler content), such as about 5% on the same basis, and the polyester typically has an acid number of 55 to 90mg KOH/gram and a specific gravity at 25°C of 0.85 to 1.1.

The polyethylene present in the composition according to the invention is generally such that it has a density of less than 0.93 grams per cubic centimetre; the polyethylene may be a linear low density polyethylene or a more contentional low density polyethylene. The ethylene-vinyl acetate copolymer typically has a vinyl acetate content not greater than 28% by weight. Either the polyethylene or the ethylene-vinyl acetate copolymer may contain a minor amount of one or more non-deleterious comonomers.

Typically, the polymer blend constitutes 10-60% by weight of the entire composition.

The hydrated mineral flame retardant present in the composition according to the invention is typically aluminium hydroxide (aluminium trihydrate), optionally together with magnesium hydroxide. When magnesium hydroxide is present, it is preferably present in an amount of 10 to 20% by weight, based on the total weight of the composition.

The flame retardant may be coated with a processing aid, such as stearic acid. The aluminium hydroxide typically has a median particle size of from 0.6 to 1 micron (such as about 0.7 microns). It preferably has a specific surface area of at least 3 cubic metre per gram (for example 7 cubic metre per gram) as measured by means of Strohlein area meter.

Preferably, the magnesium hydroxide has a crystallite size of about 0.6-0.8 microns, with a particle surface area not greater than 8 cubic metre per gram (as measured by the Brunauer Emmett Teller, or BET, method). The total proportion of flame retardant present in the composition is generally from 30 to 80% by weight (based on the total weight of the composition); a preferred proportion is 40 to 65% on the same basis.

The composition according to the invention may additionally contain additives such as antioxidants, U.V. stabilisers, lubricants, anti-hydrolysis stabilisers, carbon black and pigments. The nature and amount of such ingredients depends on the particular application of the composition.

The composition according to the invention may be blended by any suitable conventional means, for example, by mixing the components in a twin-screw extruder, a two roll mill, or a Buss KO-kneader. The resultant blend, after pelletising, may then be processed into tubes, sheets or three-dimensional articles, by extrusion or injection moulding.

The resultant artefact may be thermally cured, or cured by exposure to high energy radiation such as an electron beam or gamma radiation. When high energy radiation is used, the dose is typically in the range of 5-30 Mrads. The curable composition may contain a cross-linking agent, such as an organic peroxide (for example, dicumyl peroxide) in the polymeric composition. Such a peroxide may be used alone or in conjunction with a co-curing agent, such as a multi-functional compound, for example, triallyl cyanurate, diallylphthalate or glycol dimethacrylate. To facilitate

cross-linking during radiation, 0.2-5% by weight of a polyfunctional vinyl or allyl compound, such as triallyl cyanurate or glycol dimethacrylate, may be incorporated in the composition.

If desired, the composition may be further chemically cross-linked by the use of a polymer base onto which a silane has been grafted.

The cross-linked artefact obtained from the composition according to the invention may then be converted to a heat-unstable form, typically by heating the cross-linked heat stable artefact to about 120 to 135°C, deforming to the desired configuration and then cooling whilst in the deformed state. In use, the heat-unstable article can be recovered onto a substrate by heating sufficiently to soften the material.

A typical use of the composition according to the invention is for the protection of electrical and fibre optic cables where stringent flame resistance properties may be required. Examples of this application include the use of injection moulded articles for terminating the free ends of cables and the use of extruded tubes as conduits or as heat-recoverable sleeves.

A further possible use is for sealing of joints or damaged regions of a cable. In this application a suitably formulated composition may be processed to give a heat-unstable sheet. This can then be wrapped around the joint, or damaged cable, and recovered to provide an environmental seal. Alternatively, an extruded tube may be cut along its length to give a cylindrical sheet which is then recoverable over a cable joint.

In the aforementioned applications, artefacts made from compositions according to the invention are characterised by exceedingly low flammability, low corrosive gas evolution and smoke emission. In addition the products of pyrolysis have relatively low toxic potency.

The following examples, in which all parts and percentages are by weight, illustrate the invention.

EXAMPLE 1

<u>Ingredient</u>	<u>Function</u>	<u>%</u>
LLDPE (available from Dow Chemical under the trade name Dowlex 2552)	Polymeric base	10.0
Ethylene-vinyl acetate with a vinyl acetate content of 28% (available from Atochem under the trade name Evathane 28-05 and 28-420)	Polymeric base	22
Carbon Black (available from Carbot Plastic Ltd, under the trade name Plastlak PE1371).	U.V. Screen	2.5
Polyester oligomer (available from I.C.I. Speciality Chemicals under the trade name Hypermer FPI).	Dispersant	1
Aluminium trihydrate (available from B.A. Chemicals under the trade name of BACO SF7 S3A)	Flame Retardant	60
Antioxidant (Irganox 1010 available from Ciba Geigy)	Thermal Stabiliser	1
Polycarbodiimide (available from Bayer U.K. Ltd under the trade name Staboxal P)	Hydrolytic Stabiliser	0.5
Dicumylperoxide (available from AKZO Chemie under the trade name Perkadox BC).	Cross-linking agent	1.5
Calcium Stearate (available from Durham Chemicals Ltd)	Lubricant	1.0
Diallylphthalate (available from B.P. Chemicals Ltd)	Co-agent	0.5

The ingredients were first dry blended in a ribbon blender. The polymers were mixed with the dispersant for approximately half a minute and then the flame retardant and calcium stearate added and mixed for a further 1 minute. The remainder of the components were added and mixed for an additional 1 minute. The resulting blend was then melt-mixed in a Buss KO-kneader. Extruded strands were subsequently granulated; the granules pressed into a plaque and heat cured at 175°C in a picture frame mould. The results obtained on testing the plaque are shown in Table 1.

EXAMPLE 2

Example 1 was repeated except that 10% by weight of magnesium hydroxide was used in place of aluminium trihydrate. The magnesium hydroxide used was available from Kyowa Chemical Industry Co. Ltd (under the trade name Kisuma SB). Properties of the plaque made using this composition are given in Table 1.

EXAMPLE 3

Example 2 was repeated except that the peroxide was replaced by triallyl cyanurate. A plaque made from this composition was cured by gamma radiation until the dose received was 10 Mrad. The properties of the resulting article are given in Table 1.

EXAMPLE 4

Example 2 was repeated except that the linear low density polyethylene was replaced with a low density grade available from B.P. Chemicals under the trade name of BPD 2145. The properties for this composition, determined on a compression moulded plaque, are given in Table 1.

Property	Example			
	1	2	3	4
Tensile Strength MPa (to ASTM D412)	9	10	9	9
% Elongation at break (to ASTM D412)	340	450	340	330
Stiffness PSI (Cantilever Beam bend to ASTM D2240)	17000	19900	20000	22000
2% Secant modulus (MPa)	61	84	98	95
Resistance to fluids				
1. Hydraulic oil (Def. Stan. 91-48/1)				
Tensile Strength (MPa) after 24 hr 50°C immersion	4.0	4.5	3.8	5.0
% Elongation at break after 24 hr 50°C immersion	300	340	320	300
2. 1,1,1 trichlorethane				
Tensile Strength (MPa) after 24 hr 23°C immersion	4.0	5.0	4.5	5.5
% Elongation at break after 24 hr 23°C immersion	150	330	310	280
Limiting oxygen index (to BS 2782 Pt 1 method 141)	29	32	31	32.5
Toxicity index (to NES 713)	1.4	1.9	2.1	1.7
Temperature index (to NES 715)	240	330	300	340

Claims

1. A flame retardant polymer composition which comprises a blend of polyethylene and an ethylene-vinyl acetate copolymer having a hydrated mineral flame retardant dispersed therein, the composition further containing an oligomeric polyester resin dispersant.
2. A composition according to claim 1, in which the polyester resin is present in an amount of 1-10% by weight, based on the total filler content.
3. A composition according to claim 1 or 2, in which the polyethylene has a density less than 0.93 grams per cubic centimetre.
4. A composition according to any of claims 1 to 3, in which the ethylene-vinyl acetate copolymer has a vinyl acetate content of less than 28% by weight.
5. A composition according to any of claims 1 to 4, in which the polymer blend constitutes 10-60% by weight of the entire composition.
6. A composition according to any of claims 1 to 5, in which the hydrated mineral flame retardant is aluminium hydroxide.
7. A composition according to claim 6, in which said aluminium hydroxide has a median particle size of 0.6 to 1 micron.

8. A composition according to any of claims 1 to 7, which further comprises magnesium hydroxide.
9. A composition according to any of claims 1 to 8, in which the magnesium hydroxide has a crystalline size of 0.6 - 0.8 microns.
10. A composition according to any of claims 1 to 9, in which the total proportion of flame retardant present is 40 to 65% by weight, based on the total weight of the composition.
11. A flame retardant composition substantially as herein described in any of Examples 1 to 4.
12. A cross-linked artefact which has been produced from a composition according to any of claims 1 to 11.
13. A cross-linked artefact according to claim 12, which has thermally recovered onto a substrate by heating the artefact to a temperature above 120 degrees Celsius, deforming said artefact to the desired configuration and then cooling whilst said artefact is in the deformed state.
14. A cross-linked artefact according to claim 12 or 13, which is an injection moulding for terminating the free end of an electrical or fibre optic cable, or an extruded tube.